

The Fe L₃-edge as a probe for Fe oxide speciation

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L-edge XANES spectroscopy has been used to identify the speciation of Fe in natural samples. The majority of previous analyses are limited to the identification of Fe (II) versus Fe (III) speciation in complex natural samples however, these spectra are rarely used to identify different mineral phases in soils and sediments. Using the fine spectral variations between different crystalline and amorphous Fe phases, we developed a technique to evaluate the local co-ordination environment of Fe in natural samples. The technique makes use of splitting of the main electronic transitions in the L₃ edge (ΔE_V) region, and the ratio of their peak intensities. These spectral parameters are sensitive to the valence state, electronegativity of the coordinated ligands and the degree of distortion of the polyhedra of Fe. We collected L-edge XANES spectra of several synthetic Fe-oxides and oxyhydroxides, and also compiled the spectra of several published spectra in the literature.

When compared for the characteristic ΔE_V values and intensity ratio values; the common Fe (III) minerals, goethite, akaganeite, lepidocrocite, amorphous Fe, hematite, and maghemite fall within their own discreet oblong fields, with minor overlap between some of the phases. Similarly, the Fe (II) rich phases occupy their own positions on the plot characterized by greater intensity ratios. The differences in the characteristic intensity ratio values of the fields for the ferric standards is defined predominantly by the number of hydroxyls co-ordinating, and the characteristic ΔE_V values are governed predominantly by the magnitude of the ligand field splitting. The arrangement of the fields is also a function of the polyhedral linkages and this is reflected in the average metal-metal distances. However, this analysis is limited by the saturation effects, an artifact of the XANES analysis of thicker and Fe-rich particles.

Details of these spectral analyses, the effects of cation substitution in Fe-oxides that influence these spectral parameters, and an application of this technique to study the natural samples will be presented.

Redox stratification of the White Sea sediments

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Redox stratification is formed by the consequence of biogeochemical reactions of oxidation and reduction of organic and inorganic components of the sediments. Organic matter on the surface of the White Sea sediments is oxidized by oxygen dissolved in bottom water. However, in the subsurface horizons the oxygen is rapidly disappearing and other carriers of oxygen, namely, oxygen compounds of nitrogen, manganese, iron and sulfur serve as oxidants. The most striking manifestation of diagenesis is an extremely high content of Mn²⁺ in the pore water (sometimes more than 500 μM), which determines its flux from the sediments to the bottom water and oxidation at the contact with oxygen to form oxyhydroxides MnO₂, enriching the surface layers of the sediments. In lesser extent, migration and oxidation are characteristic of iron. After exhaustion of oxygen in the surface layer at the stage of anaerobic diagenesis newly formed oxyhydroxides (MnO₂ and FeOOH) themselves become oxidants of organic matter. Estimation of the diffusion flux of manganese from the sediments (280 $\mu\text{M}/(\text{m}^2\text{day})$) and the corresponding amount of MnO₂ formed, compared with the opposite flux of oxygen to the sediments (1-10 $\text{mM}/(\text{m}^2\text{day})$), shows that over 10% of the organic matter of the surface layer of the sediments can be oxidized with MnO₂. The role of other oxidants of organic matter (FeOOH and SO₄²⁻) is prominent in the deeper horizons. In the upper package of sediments (0 - 100 cm) 61% of the anaerobic oxidation of Corg accounted for MnO₂, the proportions of FeOOH and SO₄²⁻ are 14 and 25% respectively. At the same time in the topmost surface layer (0-5 cm) MnO₂ is practically 100 per cent oxidant agent, and at 100 cm the 100-percent oxidizer is SO₄²⁻. A detailed calculation of the balance of reduction process shows the higher consumption of organic matter in diagenesis of surface sediments than gives a direct determination of Corg. The most active processes of redox diagenesis end at 25-50cm. Layers of manganese enrichment in the deeper horizons are in the nature of metastable relics of the surface accumulation (probably, manganese nodules), subject to gradual dissipation within the sediment column.